



Studies on Divalent zinc and cadmium complexes containing 1, 2-bis (N-methylbenzimidazolyl)benzene

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Abstract

The reaction of 1,2-bis(N-methylbenzimidazolyl)benzene (N-N) with zinc and cadmium halides and perchlorates in toef-ethanol/acetone/thf yielded white/cream/pale pink complexes of the formulae $MX_2(N-N)$ [$M = Zn, X = Cl, Br$ or $I; M = Cd, X = Br$ or I], $[(CdCl_2)_{1.5}(\mu-N-N)]_2$, $[Zn(OCIO_3)(\mu-N-N)_{1.5}]_2(ClO_4)_2$ and $[Cd(OCIO_3)(\mu-N-N)_2]ClO_4 \cdot H_2O$. The complexes have been characterized based on elemental analyses, molar conductance measurements, IR, 1H and ^{13}C NMR, FAB-mass spectral studies and thermal analysis. Probable structures have been proposed.

Keywords: 1,2-bis(N-methylbenzimidazolyl)benzene, zinc and cadmium complexes, spectroscopy, thermal analysis.

1. Introduction

Benzimidazolyl derivatives and their metal complexes exhibit antibacterial, veterinary, antihelmintic, insecticidal and virucidal activities.[1] Substituents on the benzimidazolyl derivatives could

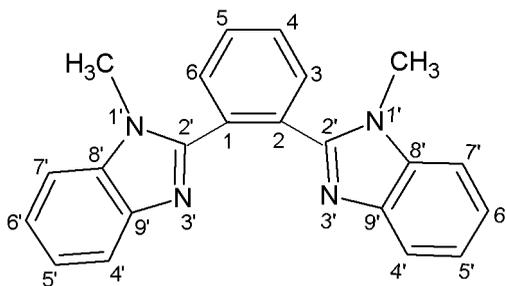
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significantly modify their reactivity towards metal ions. Further, several of their metal complexes may serve as models to mimic the active centers of metallobio-molecules.[1],[2] Divalent zinc is responsible for the function of carboxy-peptidase A and carbonic anhydrase in biological systems.[3] Thus, the coordination behavior of N-heterocycle with metal ions are of considerable importance. In this direction several transition metal complexes of 1,3-bis(benzimidazolyl/N-methylbenzimidazolyl) benzene, 1,3,5-tris(benzimidazolyl/N-methylbenzimidazolyl)benzene [4], [5]

have been synthesized and characterized from these laboratories. In continuation of the work on palladium complexes published earlier,[6] herein we report the synthesis and characterization of complexes of zinc and cadmium stabilized by 1,2-bis(N-methylbenzimidazolyl)benzene (N-N; I)



I

2. Experimental

Zinc and cadmium halides were procured from BDH. Hydrated zinc and cadmium perchlorates were prepared by dissolving zinc carbonate in 1:1 aqueous perchloric acid and evaporating the resulting solution to almost dryness under reduced pressure. The N-heterocycle, N-N was prepared according to the literature method given for related N-heterocycles.[6],[7] C, H and N analyses were carried out on a Heracus Carlo Erba 1108 microanalyser. Metal analysis was done using a Spectra AA-30 spectrometer equipped with a Varian DS-15 computer. IR (nujol mull) and Far-IR (polyethylene powder) spectra were recorded on Shimadzu IR-435 and Bruker IFS 113V spectrometers respectively. Conductivity data were obtained using a Systronics-304

Conductivity Bridge. NMR spectra were recorded in DMSO-d₆ on AMX 400 MHz spectrometer using TMS as the internal standard at SAIF, NMR Research centre, I.I.Sc., Bangalore. Thermal Analysis measurements were made on a Mettler TAHE-20 thermal analyzer with a scan rate of 5°C/min in air. The FAB-mass spectra were recorded on a JEOL SX NO₂ / DA-6000 mass spectrometer at room temperature using Argon (6 KV, 100mA) as the FAB gas at CDRI, Lucknow, India.

2.1. Synthesis

2.1.1. [ZnX₂(N-N)] (X = Cl, Br or I)(1)

To an ethanolic solution (20 ml) of the N-heterocycle (1 mmol), zinc dihalide (1 mmol) in ethanol (10 ml) was added at ambient temperature when a white/pale-pink solid separated instantaneously. It was allowed to stand for about an hour and then the solid was washed with ethanol and dried under vacuum. Yield: 68-75 %

2.1.2. [{Zn(OCIO₃)(N-N)_{1.5}}]₂(ClO₄)₂ (2)

To a THF solution (25 ml) of the N-heterocycle (3 mmol), hydrated zinc perchlorate (2 mmol) in THF (10 ml) was added. The resulting mixture was refluxed for four hours on a steam bath when a pale-pink solid separated. The solid was washed with THF and dried under vacuum. Yield: 75 %

2.1.3. [(CdCl₂)_{1.5}(N-N)]₂ (3)

To an ethanolic solution (15 ml) of the N-heterocycle (2 mmol), cadmium chloride (3 mmol) in ethanol-teof(triethylorthoformate) (10:5 ml) was added. The resulting mixture was refluxed for an hour on a steam bath when a white solid separated. The solid was washed with ethanol and dried under vacuum. Yield: 70%

2.1.4. [CdX₂(N-N)] (X = Br or I) (4)

To an ethanolic solution (15 ml) of the N-heterocycle (1 mmol), cadmium dihalide (1 mmol) in ethanol-teof (10:5 ml) was added.

The resulting mixture was refluxed for four hours on a steam bath when a white/cream coloured solid separated. The solid was washed with ethanol and dried under vacuum. Yield: $[\text{CdBr}_2(\text{N-N})]$ 72%, $[\text{CdI}_2(\text{N-N})]$ 75%

2.1.5. $[\text{Cd}(\text{OCIO}_3)(\text{N-N})_2]\text{ClO}_4 \cdot \text{H}_2\text{O}$ (5)

To an acetone solution (15 ml) of the N-heterocycle (2 mmol), hydrated cadmium perchlorate (1 mmol) in acetone-TEOF (10:5 ml) was added. The resulting mixture was refluxed for four hours on a steam bath when a cream coloured solid separated. The solid was washed with acetone and dried under vacuum. Yield: 75 %.

3. Results and Discussion

The halides and perchlorates of zinc and cadmium react with 1,2-bis(N-methylbenzimidazolyl)benzene (N-N) in 1:1 mole ratio in ethanol/acetone/THF to produce complexes of the formulae $\text{MX}_2(\text{N-N})$ ($\text{M} = \text{Zn}$, $\text{X} = \text{Cl}$, Br or I ; $\text{M} = \text{Cd}$, $\text{X} = \text{Br}$ or I), $[(\text{CdCl}_2)_{1.5}(\text{N-N})_2]$, $[\text{Zn}(\text{OCIO}_3)(\text{N-N})_{1.5}]_2(\text{ClO}_4)_2$ and $[\text{Cd}(\text{OCIO}_3)(\text{N-N})_2]\text{ClO}_4 \cdot \text{H}_2\text{O}$. The complexes are insoluble in common organic solvents but are soluble in dimethylformamide in which the halo complexes are non-electrolytes. The zinc and cadmium perchlorate complexes show 1:2 and 1:1 electrolytic behavior in DMF respectively.[8]-[10] The physical properties and analytical results of the complexes are listed in Table 1.

The nujol mull IR spectrum of 1,2-bis(N-methylbenzimidazolyl)benzene exhibits $\nu_{\text{C}=\text{C}}$ and $\nu_{\text{C}=\text{N}}$ at 1616 cm^{-1} . A peak observed at 1403 cm^{-1} is assigned to the symmetrical deformation mode of N- CH_3 group. The bands at 1290, 1010 and 964 cm^{-1} are assigned to the benzimidazole ring vibrations. The infrared spectra of the metal complexes are comparable to those of the uncoordinated N-heterocycle except for minor shifts in the positions of some of the bands. The $\nu_{\text{C}=\text{C}}$ and $\nu_{\text{C}=\text{N}}$ have appeared as weak bands around 1630 and 1610 cm^{-1} respectively. Symmetrical deformation mode of methyl group of N- CH_3 is observed around 1410 cm^{-1} . The IR spectral data of the complexes are suggestive of coordination of the heterocycle via the tertiary nitrogens of the benzimidazole moiety.[10]-[13] The perchlorate complexes in addition to the

heterocycle bands exhibited peaks around 1100 and 620 cm^{-1} . The former peak is split (Table 1) implying monodentate coordination of the perchlorate group. IR spectral and conductivity data of the perchlorate complexes suggest that one of the perchlorate groups is coordinated to the metal and the other is ionic in nature. Far-IR spectrum of $[(\text{CdCl}_2)_{1.5}(\text{N-N})]_2$ recorded in polyethylene powder indicates the presence of both bridging(b) and terminal(t) chlorides,[14]-[19] $\nu_{\text{Cd-Cl(b)}}$ being at 315 and $\nu_{\text{Cd-Cl(t)}}$ at 349 cm^{-1} . The FAB-mass spectra of $[\text{Zn}_2(\text{OCIO}_3)_2(\text{N-N})_3](\text{ClO}_4)_2$ and $[(\text{CdCl}_2)_{1.5}(\text{N-N})]_2$ have supported the binuclear and trinuclear nature respectively of the complexes.[20],[21] The molecular ion peak m/z , 1348 which corresponds to $[\text{Zn}_2(\text{ClO}_4)_2(\text{N-N})_3]^{2+} + 3\text{H}^+$ supports the dimeric nature of the complex. The other peaks (m/z) due to the fragmentation species $\text{Zn}_2(\text{ClO}_4)(\text{N-N})_2$ (907), $\text{Zn}(\text{ClO}_4)(\text{N-N})_2$ (841), $\text{Zn}_2(\text{ClO}_4)(\text{N-N})$ (568), $\text{Zn}(\text{ClO}_4)(\text{N-N})-2\text{H}^+$ (501), $\text{Zn}((\text{N-N})-2\text{H}^+)$ (402) are also observed. In addition, a weak peak due to the association of fragments is observed at m/z , 1172 corresponding to $\text{Zn}_3(\text{ClO}_4)_3(\text{N-N})_2-\text{H}^+$. The mass spectrum of $[(\text{CdCl}_2)_3(\text{N-N})_2]$ does not show molecular ion peak due to $\text{Cd}_3\text{Cl}_6(\text{N-N})_2$ but a peak at 1138 is observed and this corresponds to $\text{Cd}_3\text{Cl}_4(\text{N-N})[(\text{N-N})-\text{CH}_3]-2\text{H}^+$. Other peaks with m/z values 1007, 825, 787 and 487 correspond to fragmented species $\text{Cd}_2\text{Cl}_3(\text{N-N})_2$, $\text{CdCl}(\text{N-N})_2$, $\text{Cd}(\text{N-N})_2-2\text{H}^+$ and $\text{CdCl}(\text{N-N})$ respectively. In addition, peaks at m/z 1193 and 941 are attributed to the associated fragments $\text{Cd}_3\text{Cl}_5(\text{N-N})_2 + 2\text{H}^+$ and $\text{Cd}_2\text{Cl}(\text{N-N}) + 2\text{H}^+$ respectively.

The ^1H NMR spectrum of the N-heterocycle (I) in DMSO-d_6 exhibits a multiplet at δ 7.8 due to benzene ring protons (H-3-6). Further, the spectrum reveals that the protons of the two benzimidazole moieties of the heterocycle are equivalent. The resonances due to H-4' and H-7' are observed as doublets at δ 7.50 and 7.47 respectively and the signals due to H-5' and H-6' as triplets at δ 7.20 and 7.14 respectively. The N- CH_3 resonance is at δ 3.48 as a singlet. The PMR spectra of the zinc and cadmium complexes exhibit peaks, due to coordinated heterocycle and these have undergone minor shifts as compared to those of uncoordinated N-heterocycle (Table 2).[22]

Table 1. Analytical data and i.r spectral data of zinc and cadmium complexes

Compound	Color	M. p. (°C)	Λ^a ($\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$)	Found (calcd.%)				I.r. Spectral data (cm^{-1})		
				Zn/Cd	C	H	N	$\delta_{\text{N-CH}_3}$	$\nu_{\text{C=C}} \& \nu_{\text{C=N}}$	ν_{ClO_4}
N-N	White	250	-	-	78.08, (78.14)	5.36, (5.37)	16.56, (16.11)	1403	1545,1616	
[ZnCl ₂ (N-N)]	Pale-pink	>280	5	13.77, (12.90)	55.66, (55.54)	3.80, (2.89)	11.80, (10.69)	1398	1538,1610	
[ZnBr ₂ (N-N)]	Pale pink	> 270	9	11.59, (12.00)	46.88, (47.35)	3.21, (3.34)	9.94, (9.89)	1409	1545,1610	
[ZnI ₂ (N-N)]	White	> 280	18	9.94, (10.50)	40.18, (39.35)	2.75, (2.66)	8.50, (7.52)	1409	1538,1621	
[{Zn(OCIO ₃)(N-N) _{1.5} }] ₂ (ClO ₄) ₂	Pale-pink	>280	150	8.50, (9.80)	51.34, (52.03)	3.39, (3.53)	10.89, (10.25)	1403	1538,1610	1134,1072 (ν_3) 622 (ν_4)
[(CdCl ₂) _{1.5} (N-N)] ₂	White	>250	11	27.54, (26.98)	43.10, (44.00)	2.96, (3.70)	9.10, (7.50)	1403	1545,1626	
[CdBr ₂ (N-N)]	Cream	>250	12	18.42, (18.31)	43.30, (43.50)	3.00, (2.91)	9.20, (8.15)	1403	1546,1621	
[CdI ₂ (N-N)]	White	>250	13	15.95, (15.67)	37.50, (37.80)	2.90, (2.92)	8.00, (7.90)	1409	1545,1621	
[Cd(OCIO ₃)(N-N) ₂] ₂ ClO ₄ . H ₂ O	Cream	>250	97	11.37, (11.10)	52.52, (52.90)	3.80, (4.00)	10.96, (9.70)	1409	1548,1616	1098,1062 (ν_3) 628 (ν_4)

^aMolar conductance of ca. 10⁻³ M solution in DMF

Table 2. ¹H NMR chemical shifts (ppm) for the N-heterocycle and complexes.

Compound ^a	Benzene ring*		Benzimidazole ring*				
	H-3,6	H-4,5	H-4'	H-5'	H-6'	H-7'	N-CH ₃
N-N	7.80 m	7.80 m	7.50 d	7.20 t	7.14 t	7.47 d	3.48 s
[ZnCl ₂ (N-N)]	7.96 cm (0.16)	7.88 cm (0.08)	8.33 cm (0.83)	7.38 cm (0.18)	7.38 cm (0.24)	7.22 cm (-0.25)	3.34 s (-0.14)
[ZnBr ₂ (N-N)]	8.0 cm (0.20)	7.90 cm (0.10)	7.80 cm (0.30)	7.40 cm (0.20)	7.40 cm (0.26)	7.80 cm (0.33)	3.76 s (0.28)
[ZnI ₂ (N-N)]	7.89 cm (0.09)	7.89 cm (0.09)	7.65 cm (0.15)	7.32 cm (0.12)	7.32 cm (0.18)	7.65 cm (0.18)	3.34 s (-0.14)
[[Zn(OCIO ₃)(N-N) _{1.5}] ₂ (ClO ₄) ₂]	7.87 cm (0.07)	7.82 cm (0.02)	7.60 cm (0.10)	7.25 cm (0.05)	7.25 cm (0.11)	7.56 cm (0.09)	3.56 s (0.08)
[(CdCl ₂) _{1.5} (N-N)] ₂	7.86 cm (0.06)	7.84 cm (0.04)	7.56 d (0.06)	7.25 t (0.05)	7.22 t (0.08)	7.56 d (0.09)	3.58 s (0.10)
[CdBr ₂ (N-N)]	7.87 cm (0.07)	7.84 cm (0.04)	7.54 cm (0.04)	7.23 cm (0.03)	7.23 cm (0.09)	7.54 cm (0.07)	3.57 s (0.09)
[CdI ₂ (N-N)]	7.86 cm (0.06)	7.84 cm (0.04)	7.50 cm (0.00)	7.25 cm (0.05)	7.25 cm (0.11)	7.56 cm (0.09)	3.58 s (0.10)
[Cd(OCIO ₃)(N-N) ₂]ClO ₄ .H ₂ O	7.82 cm (0.02)	7.82 cm (0.02)	7.58 cm (0.08)	7.27 cm (0.13)	7.27 cm (0.13)	7.58 cm (0.11)	3.62 s (0.14)

^a Spectra recorded in dms_o-d₆: s: singlet; d: doublet; t: triplet; m: multiplet; cm: complex multiplet

*Values in parentheses are coordination induced shifts: c.i.s = $\delta_{\text{complex}} - \delta_{\text{ligand}}$

Table 3. ^{13}C NMR chemical shifts (ppm) for the N-heterocycle and complexes.

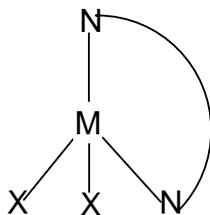
Compound ^a	Benzene ring*			Benzimidazole ring*							
	C-1,2	C-3,6	C-4,5	C-2'	C-4'	C-5'	C-6'	C-7'	C-8'	C-9'	N-CH ₃
N-N	130.75	131.33	129.98	152.18	118.96	122.20	121.65	110.30	135.60	142.38	30.63
[ZnCl ₂ (N-N)]	127.82 (-2.93)	132.26 (0.93)	130.60 (0.62)	151.46 (-0.72)	118.20 (-0.76)	123.82 (1.62)	123.82 (2.17)	111.39 (1.09)	134.61 (-0.99)	134.61 (-7.77)	31.80 (1.17)
[ZnBr ₂ (N-N)]	127.82 (-2.93)	132.26 (0.93)	130.93 (0.95)	151.81 (-0.37)	118.40 (-0.56)	124.14 (1.94)	123.62 (1.97)	111.65 (1.35)	134.91 (-0.69)	134.91 (-7.47)	31.97 (1.34)
[ZnI ₂ (N-N)]	127.90 (-2.85)	132.30 (0.97)	130.80 (0.82)	151.67 (-0.51)	118.0 (-0.96)	123.90 (1.70)	123.40 (1.75)	111.50 (1.20)	134.80 (-0.80)	139.10 (-3.28)	31.86 (1.23)
[[Zn(OCIO ₃)(N-N) _{1.5}]] ₂ (ClO ₄) ₂	128.34 (-2.41)	132.30 (0.97)	131.73 (1.75)	152.20 (0.02)	119.05 (0.09)	124.73 (2.53)	124.73 (3.08)	112.24 (1.94)	135.62 (0.02)	139.98 (-2.40)	32.36 (1.73)
[[CdCl ₂] _{1.5} (N-N)] ₂	129.00 (-1.75)	132.00 (0.67)	130.40 (0.42)	151.30 (-0.88)	119.40 (0.44)	123.20 (1.0)	122.50 (0.85)	110.90 (0.60)	134.90 (-0.70)	140.30 (-2.08)	31.60 (0.97)
[CdBr ₂ (N-N)]	129.20 (-1.55)	132.00 (0.67)	130.40 (0.42)	151.50 (-0.68)	119.20 (0.24)	123.10 (0.90)	122.40 (0.75)	110.90 (0.60)	135.00 (-0.60)	140.50 (-1.88)	31.30 (0.67)
[CdI ₂ (N-N)]	129.20 (-1.55)	132.00 (0.67)	130.50 (0.52)	151.70 (-0.48)	119.00 (0.04)	123.20 (1.0)	122.50 (0.85)	111.00 (0.70)	135.00 (-0.60)	140.50 (-1.88)	31.30 (0.67)
[Cd(OCIO ₃)(N-N) ₂]ClO ₄ .H ₂ O	128.20 (-2.55)	132.10 (0.77)	130.10 (0.12)	151.60 (-0.58)	119.40 (0.44)	124.40 (2.20)	122.50 (0.85)	111.00 (0.70)	134.90 (-0.70)	139.40 (-2.98)	31.60 (0.97)

* Values in parentheses are coordination induced shifts: c.i.s = $\delta_{\text{complex}} - \delta_{\text{ligand}}$

The ^{13}C NMR spectrum of the N-heterocycle exhibits ten signals in the range of δ 110.0–158.4 except that of N-CH₃ which is at δ 30.63. The assignments of the signals are made with the aid of off-resonance decoupled spectrum of the heterocycle and literature reports (Table 3).[23]-[25] The resonances due to C-8' and C-9' in the coordinated heterocycle are shifted upfield. The other carbon signals are shifted either upfield or downfield relative to those of the uncoordinated N-heterocycle. The coordination induced shifts, (c.i.s = $\delta_{\text{complex}} - \delta_{\text{ligand}}$) are negative for upfield and positive for downfield shifts. The negative c.i.s may be attributed to greater metal-to-ligand π -back donation whereas positive c.i.s to ligand-to-metal σ -donation.[26]

The thermogravimetric analysis (TGA) of the complex, [Cd(OCIO₃)(N-N)₂]ClO₄.H₂O, shows a weight loss in the range 80-100° C and this corresponds to the loss of a water molecule implying its hydrated nature.[27],[28]

The analytical data, IR, ^1H and ^{13}C nmr spectral results have indicated that the N-heterocycle is coordinated to the metal ion. The N-heterocycle is planar and can serve as chelating or bridging bidentate ligand. In the case of MX₂(N-N) (M = Zn or Cd) complexes, the tertiary nitrogen of each benzimidazole unit and the halides are coordinated to the metal. Hence the complexes are proposed a tetrahedral geometry (II) in which the N-heterocycle acts as a chelating bidentate ligand.



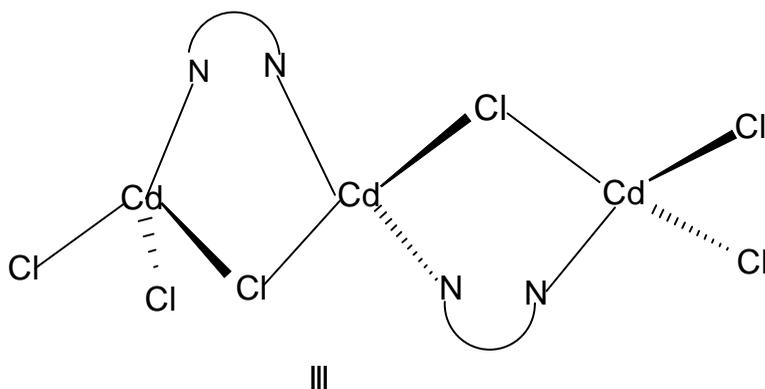
II

M = Zn: X=Cl, Br or I

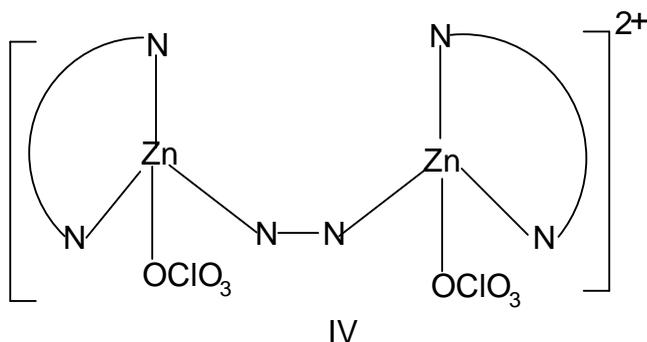
M = Cd; X = Br or I

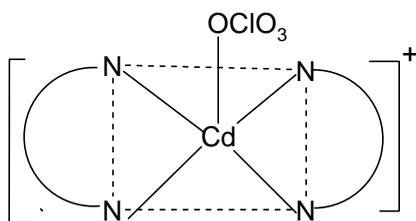
The far-IR spectrum of the [(CdCl₂)_{1.5}(N-N)]₂ complex indicated the presence of both bridging and terminal halides. The FAB-mass spectrum of [(CdCl₂)_{1.5}(N-N)]₂ has supported the trinuclear nature of the complex. Based on these results, together with IR, NMR

spectral studies, the complex may be assigned, trinuclear structure (III) with each cadmium having tetrahedral environment involving heterocycle and chloride bridges. A similar bidentate bridging of the N-heterocycle is proposed in the complex $[\text{Pd}(\text{cotl})\text{Br}]_2(\mu\text{-N-N})[6]$ (cotl = cyclooctenyl).

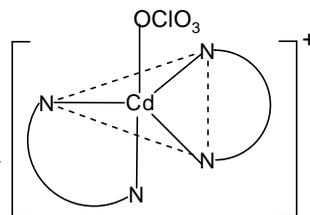


Based on FAB-MS, conductivity and spectral data, the zinc perchlorate complex cation is suggested to have a binuclear structure (IV) with a tetrahedral environment around each metal ion involving bidentate bridging heterocycle, whereas the cadmium perchlorate complex cation a mononuclear structure with square pyramidal (V) or trigonal bipyramidal geometry (VI) around the metal ion.





V



VI

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